

VI.8 High Temperature Fuel Cells for Cogeneration of Chemicals and Electricity

Objectives

- Determine the thermal self-sustainability, temperature gradients, electrical output, product composition, efficiency, and syngas productivity of a methane electrochemical partial oxidation (EPOx) reactor.
- Develop methods to avoid coking, and prove that excellent stability against coking can be achieved during long-term operation.
- Explore the use of alternative anode materials in order to eliminate coking with methane and other hydrocarbons and also allow redox cycling.
- Evaluate the technical and economic viability of the proposed technology based on the above information.

Accomplishments

- We have shown that a change in the gas flow geometry of the SOFC tests yields an improvement in methane conversion to syngas from approximately 70% to over 90%. This is significant because it proves the EPOx SOFC reactors can provide very high conversion to syngas.
- Modeling results (in collaboration with Professor Robert Kee at Colorado School of Mines) have shown that adding an anode barrier layer can keep the Ni-YSZ anode completely outside of the thermodynamic coking range. This is important because it demonstrates that this geometry can be expected to provide stable operation over long time periods.
- Substantial increase in the cell stability parameter range (critical current decrease by a factor of approximately 2 times) was demonstrated by adding

small amounts (approximately 20%) of air or CO₂ to the methane fuel feed.

Introduction

In the first year of this Phase I project, we have demonstrated the feasibility of combined chemical and electricity cogeneration using solid oxide fuel cells (SOFCs). Suitable operating conditions were established for doing electrochemical partial oxidation of natural gas that produced maximum electrical power output while providing maximum conversion of the fuel to synthesis gas (H₂+CO). The problem of coke formation on the SOFC anodes was addressed, with a new barrier layer approach and changes in fuel composition shown to increase the parameter range for stable coke-free operation.

This approach has significant potential economic advantages. That is, when SOFCs become cost effective for electricity generation, the syngas becomes a low-cost by-product. This could provide an important new route to low-cost hydrogen and gas-to-liquid fuels. From another perspective, the ability to sell both electricity and chemicals increases the value of the SOFCs, improving their prospects for commercialization.

Approach

Extensive electrical testing of anode-supported SOFCs with methane fuel was done in combination with gas chromatograph and mass spectrometer measurements of reaction products for a range of conditions. While these were single-cell tests, the cell area and current were large enough to achieve partial oxidation stoichiometry (O²/CH₄ ≈ 1) for reasonable fuel flow rates. Cell stability was tested versus operating conditions, additions of H₂O/CO₂ to the methane, and catalyst/barrier layers. Successful testing for over 300 hours was also carried out. These experiments provided the experimental proof that SOFCs can act as effective devices for cogenerating electricity and syngas.

Detailed modeling was carried out in collaboration with Colorado School of Mines, providing detailed predictions of gas composition gradients within the anode and anode flow field. The work focused on the effect of anode barrier layers on overall cell/stack performance and changes in the gas composition within the Ni-YSZ anode that influence anode coking. Most model input parameters were quantitatively established by structural evaluation of the SOFCs and barriers

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combined with calibration experiments on the SOFCs prior to methane testing. These experiments provided a compelling explanation for how direct-methane SOFCs can work without coking, and also a means for predicting conditions for stable SOFC operation.

Results

Extensive cell electrical testing showed results as expected for anode-supported SOFCs operated with methane fuel [1]. For example, at 750°C and 0.7 V, the current density was 0.8 A/cm² and the power density was 0.57 W/cm². Differentially pumped mass spectra from the SOFC anode gas stream (Figure 1) showed a decrease in methane-related (mass 16) peaks and an increase in hydrogen (mass 2) and CO (mass 28) with increasing SOFC current density. (Note that the methane flow rate was fixed such that the ratio O^2/CH_4 was proportional to the current density.) H_2 and CO reached maximum values at $O^2/CH_4 \approx 0.7$ before decreasing with further increases in O^2/CH_4 . The CO_2 content (mass 44) remained low at low O^2/CH_4 but then increased more rapidly when O^2/CH_4 increased above 0.7.

These trends agree with the equilibrium thermodynamic prediction, except that CH_4 did not decrease to zero at large O^2/CH_4 , and the peak H_2 and CO content appears well below the predicted value $O^2/CH_4 = 1$. Both these differences can be explained if a fraction of inlet CH_4 flow does not react, possibly due to the flow geometry of our SOFC test. In order to test the above idea, we did additional experiments with an altered geometry where all the CH_4 flowed over the full radius (approximately 1 cm) of the anode. Figure 2 shows schematically the original and new geometries and plots the methane utilization versus O^2/CH_4 for both cases. The methane utilization saturates at approximately 70% for the original geometry,

but for the altered geometry increases continuously to approximately 90% with increasing O^2/CH_4 to 1. In the new geometry, the H_2 and CO mass spectrometer peaks increase continuously with increasing O^2/CH_4 in this range, in better agreement with the thermodynamic prediction. The maximum measured syngas production rate estimated based on mass spectrometer sensitivities was approximately 20 sccm cm⁻².

Taken together, the above results demonstrate that a direct-methane SOFC can work very effectively for both producing electricity and converting methane to syngas.

In order to maintain thermal balance in an EPOx SOFC, it may be useful to operate at voltage (V) values as low as 0.4 V. Electrical test results show the low voltage actually provides higher power density than $V = 0.7$ V. Another advantage of lower V is that decreasing from a typical SOFC $V = 0.7$ V to 0.4 V approximately doubles J . That is, the oxygen ion current density and the syngas production rate are approximately doubled. However, this way of operating a SOFC, with pure methane fuel, low V, and high current density, is unusual, so it is important to demonstrate that the cells can operate stably. Endurance tests carried out on a number of cells showed stable operation. Figure 3 shows an example of a SOFC life test conducted for over 300 hours. The test was carried out with an anode catalyst layer using dry methane at 30 sccm, $O^2/CH_4 = 0.82$, $V \approx 0.4$ V, and 750°C. The SOFC showed a slight performance decrease during the first 150 hours (which is not unusual for SOFCs), followed by stable operation for the final 200 hours. Subsequent scanning electron microscopy-energy dispersive x-ray spectroscopy observations showed that no carbon was present on the anode.

We have been fortunate to develop a collaboration with Professor Robert Kee at Colorado School of Mines, who has well-developed models that account for the

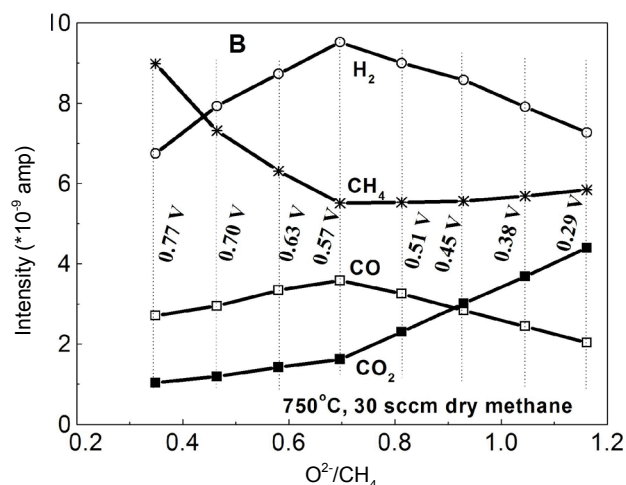


FIGURE 1. Product Gas Composition versus Oxygen to Methane Ratio

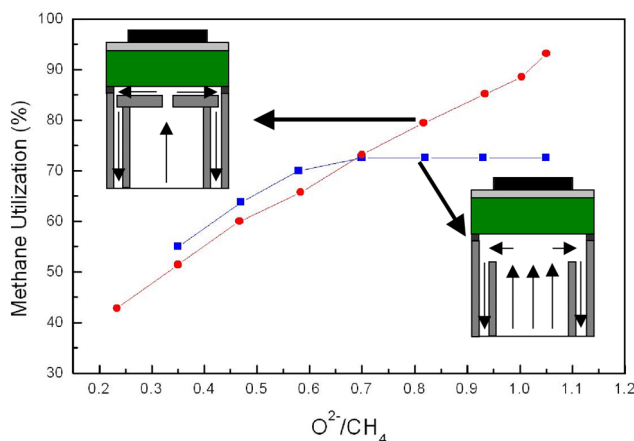


FIGURE 2. Comparison of Methane Utilization versus Oxygen to Methane Ratio for Two Gas Flow Geometries

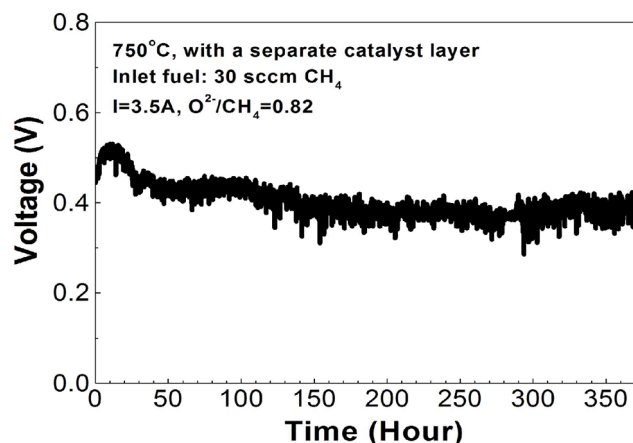


FIGURE 3. SOFC Stability Test during Methane EPOx Operation

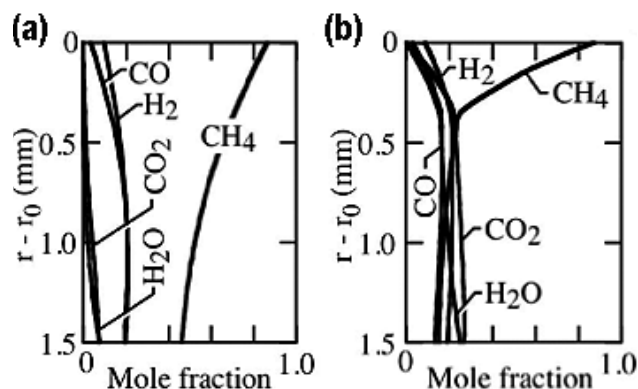


FIGURE 4. Calculated Gas Composition versus Position during Direct-Methane SOFC Operation within the Ni-YSZ Anode (a) and a Ni-YSZ Anode with a 0.3 mm Thick Barrier Layer (b)

details of flow, reactions, and electrochemistry within the anode compartment of a SOFC. Detailed structural information (e.g., layer thicknesses, porosities) measured from the specific SOFCs, along with known reaction rates on Ni-YSZ anodes, are input in order to make the results more quantitative. Further model calibration of gas transport within the anode microstructure was achieved by matching the calculations to experimental cell calibration measurements in different hydrogen-steam mixtures.

The simulation was then applied to methane operation, using the above anode information as well as prior data on reforming reaction rates within Ni-YSZ anodes. Some of the results are shown in Figure 4, which compares a case of a conventional Ni-YSZ anode (Figure 4a) with a Ni-YSZ anode with a 0.3 mm thick zirconia barrier layer (Figure 4b) [2]. The figures show the gas composition profile from the gas flow side (top) to the electrolyte (bottom). In Figure 4a, the decrease in CH_4 content approaching the electrolyte side is seen,

along with an increase in the products H_2O and CO_2 . With the barrier layer, the methane content within the Ni-YSZ portion is substantially decreased, whereas the products H_2O and CO_2 tend to be trapped in the anode. The overall result is that the fuel composition in the Ni-YSZ anode is kept outside of the equilibrium coking range. This is an important result helping to explain how direct-methane SOFCs can maintain stable operation.

Experiments have been done to determine the effects of adding small amounts (approximately 20%) of air or CO_2 to the methane fuel. Initial results suggest that the additions increase the parameter range for stable coke-free operation.

Conclusions and Future Directions

The above cell test and mass spectrometer results demonstrate that direct-methane SOFCs can effectively produce electricity and convert methane to syngas. Cell stability testing has continued to help delineate the stable operation range for SOFCs with methane fuel. Model calculations of the anode compartment in SOFCs have also been important for understanding how anode barrier layers allow stable operation by keeping the Ni-YSZ anode outside of the equilibrium coking range.

In future work, we will continue ongoing work on cell stability, including effects of barrier layers and modifications of the fuel composition (i.e., adding small amounts of air, steam, or CO_2). Note that the work with air will also serve to show the effects of contamination in natural gas. We will also conduct tests with simulated natural gas containing realistic amounts of ethane and propane. Other experiments will include testing of ceramic anode SOFCs, more long-term testing, and testing of larger-area devices.

Simulation work will continue in order to obtain more accurate predictions of gas composition and temperature gradients within the anode, as well as overall stack performance. The simulations will also be carried out with air addition to methane, suitable for improving thermal balance in stand-alone reactors, and with steam/ CO_2 addition, suitable for use in tandem with a source of heat and steam/ CO_2 such as a coal gasifier. Decisions will be made as to the best operating conditions for free-standing devices versus devices operated with an external source, and the best catalyst/barrier layer combination will be selected.

FY 2006 Publications/Presentations

1. Zhongliang Zhan, Yuanbo Lin, Manoj Pillai, Ilwon Kim, Scott A Barnett, "High-Rate Electrochemical Partial Oxidation of Methane in Solid Oxide Fuel Cells," J. Power Sources, in press.

2. Huayang Zhu, Andrew M. Colclasure, Robert J. Kee, Yuanbo Lin, Scott A. Barnett. "Anode Barrier Layers for Tubular Solid-Oxide Fuel Cells with Hydrocarbon Fuel Streams," J. Power Sources, in press, 2006.
3. Robert J. Kee, Huayang Zhu, Andrew M. Colclasure, Yuanbo Lin, and Scott A. Barnett, "Tubular Solid-Oxide Fuel Cells Using Either Anode Recycle or Barrier Layers," Proceedings of the 7th European Fuel Cell Forum, Ulf Bossel, Editor, Paper Number B074, 2006.
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5. Scott A. Barnett, "Energy Applications of Solid Oxide Fuel Cells," 2006 Taiwan – Midwest-USA Symposium on Science and Engineering, Evanston, IL, June, 2006.
6. Scott A. Barnett, "Solid Oxide Fuel Cells: New Materials and New Applications," Montana State University, Bozeman, MT, March, 2006.
7. Yuanbo Lin, Zhongliang Zhan, Ilwon Kim, Scott A. Barnett, "Co-Production of Hydrogen/Syngas and Electricity by Direct-Methane Solid Oxide Fuel Cells," American Ceramic Society Meeting, Cocoa Beach, January, 2005.
8. Scott A. Barnett, "Solid Oxide Fuel Cells: New Materials and New Energy Alternatives," Carnegie-Mellon University, Dept. of Materials Science colloquium, December, 2005.
9. Scott A. Barnett, "Solid Oxide Fuel Cells and the Hydrogen Economy," Colorado School of Mines, Chemical Engineering Department, December, 2005.

References

1. Y. Lin, Z. Zhan, J. Liu, and S.A. Barnett, "Direct Operation of Solid Oxide Fuel Cells with Methane Fuel," Solid State Ionics, 176, 1827-1835 (2005).
2. Y. Lin, Z. Zhan, and S.A. Barnett, "Improving the Stability of Direct-Methane Solid Oxide Fuel Cells Using Anode Barrier Layers," Journal of Power Sources, In Press.